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A note on rotational isomerism of β-chloropropionyl chloride in the liquid state

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From analyses of the liquid state infrared absorption spectra in 550-750 cm^{-1} region of some acyl halides Katon & Feairheller (1966) concluded that there are two stable isomeric forms in propionyl halides in the liquid phase and the number of such rotamers in liquid *n*-butyryl halides is four. Further, though acetyl halides have only one molecular configuration, molecules of haloacetyl halides (Nakagawa *et al* 1952, Jenkins & Ladd 1968) are found to exist as trans and gauche isomers in the liquid state. Hence, the molecules of β-chloro propionyl chloride should have more than two stable isomeric forms in the liquid phase as in *n*-butyryl chloride. In order to investigate this point, the Raman and infrared spectra of β-chloropropionyl chloride in liquid phase have been studied and the analysis of the relevant data are presented in this note.

The molecules of β-chloropropionyl chloride can exist in five different isomeric forms. Of these there are two configurations where the COCl and CH_2Cl groups are in the gauche positions and in one of them the two chlorine atoms in these two groups are very close to each other. From energetic considerations this form has been excluded (cf, Brown & Sheppard, 1955) and accordingly, β-chloro-propionyl chloride should exist in four stable isomeric configurations in the liquid state as has been reported in the case of *n*-butyryl chloride (Katon & Feairheller, 1966). The vibrational spectra of β-chloropropionyl chloride should, therefore exhibit eight C—Cl stretching vibration frequencies, two for each of the four conformers.

In acetyl chloride (Overend *et al* 1961) the C—Cl stretching vibration frequency is at 590 cm ^{1} but in liquid chloroacetyl chloride (Nakagawa *et al* 1952) there are four C—Cl stretching vibrations at somewhat higher frequency regions *viz.*, 620—780 cm^{-1}. In propionyl chloride such frequencies in the gauche and trans forms in the liquid state are 563 ad 698 cm^{-1} respectively and in n-butyryl chloride the four vibrations have been found between 560-724 cm^{-1} (Katon & Feairheller 1966). In β-chloropropionyl chloride the eight C—Cl stretching vibrations are expected to appear in the region 600-800 cm^{-1} in the liquid phase vibrational spectra.

In the Raman spectrum of β-chloropropionyl chloride in the liquid phase there are three frequency shifts at 615, 673 and 763 cm ^{1} while in its infrared spectrum three strong bands at 668, 674 and 688 cm^{-1}, a medium strong band at 705 cm^{-1} and two weak bands at 740 and 760 cm ^{1} are observed. All these bands 615, 668, 673, 688, 705, 740 and 760 cm^{-1} occur in the region corresponding to the C—Cl stretching vibrations and in all probability account for seven of the eight C—Cl stretchings for the four expected isomers of β-chloropropionyl chloride.

The carbonyl stretching vibration frequencies, in favourable cases, may be used to identify the stable conformers in molecules containing the C = O group. Thus, in sym. dichloroacetone (Bellamy & Williams 1957) and in sym. dibromo- and diiodoacetones (Crowder & Smyrl 1971) three vibrational frequencies corresponding to modes involving stretching of the C = O bond have been reported in the spectrum of the liquid in each case, thereby indicating the existence of three rotational isomers in these molecules. In the present molecule of β-chloropropionyl chloride in the liquid phase three Raman bands at 1619, 1757 and 1780 cm ^{1} have been observed. The infrared spectrum of the liquid on the other hand shows a strong and broad band at 1780 cm ^{1} and two weak bands at 1612 and 1650 cm ^{1}. The four bands 1619, 1650, 1757 and 1780 cm^{-1} represent the frequencies of the C = O stretching vibration in the four isomeric forms of the molecules. All these results indicate that the molecules of β-chloropropionyl chloride in the liquid phase exist in four stable isomeric configurations.

References

Bellamy L. J. & Williams R. L. 1957 *J. Chem. Soc.*, 4294.

Brown J. K. & Sheppard N. 1955 *Proc. Roy. Soc.* **A231**, 555.

Crowder G. A. & Smyrl N. 1971 *J. Mol. Structure* **7**, 478.

Jenkins J. E. F. & Ladd J. A. 1968 *J. Chem. Soc.* **B**, 1237.

Katon J. E. & Gearheller (Jr.) W. R. 1966 *J. Chem. Phys.* **44**, 144.

Nakagawa I, Ichisima I., Kuratani K., Shimanouchi T. & Mizushima S. 1952 *J. Chem. Phys.* **20**, 1720.

Overend J., Nyquist R. A., Evans J. C. & Potts W. J. 1961 *Spectrochim. Acta* **17**, 1205.